Median dual cell 3D

August 22, 2007

1 Equations

1.1 Mass conservation

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla}.\vec{N}_i + R_i \tag{1}$$

with

$$\vec{N}_i = c_i\vec{v} - \sum_j D_{ij}\vec{\nabla}c_j - w_i c_i \vec{\nabla}U \tag{2}$$

1.2 Poisson's equation

$$\vec{\nabla}^2 U + \frac{F}{\epsilon}\sum_i z_i c_i = 0 \tag{3}$$

1.3 Butler-Volmer kinetics

$$v = k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]c_{red} - k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]c_{ox} \tag{4}$$

2 Element matrix

2.1 Convection

2.1.1 Fluctuation in node

$$\Delta c_i^m = \int_{V^m} -\vec{v}.\vec{\nabla}c_i dV$$

2.1.2 Element contribution to fluctuation in node

$$\vec{\mathcal{V}}^1 = 75\vec{v}^1 + 23\vec{v}^2 + 23\vec{v}^3 + 23\vec{v}^4$$

$$\vec{\mathcal{V}}^2 = 23\vec{v}^1 + 75\vec{v}^2 + 23\vec{v}^3 + 23\vec{v}^4$$

$$\vec{\mathcal{V}}^3 = 23\vec{v}^1 + 23\vec{v}^2 + 75\vec{v}^3 + 23\vec{v}^4$$

$$\vec{\mathcal{V}}^4 = 23\vec{v}^1 + 23\vec{v}^2 + 23\vec{v}^3 + 75\vec{v}^4$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array} \right\} = \frac{1}{1728} \left[\begin{array}{cccc} \vec{\mathcal{V}}^1.\vec{n}^1 & \vec{\mathcal{V}}^1.\vec{n}^2 & \vec{\mathcal{V}}^1.\vec{n}^3 & \vec{\mathcal{V}}^1.\vec{n}^4 \\ \vec{\mathcal{V}}^2.\vec{n}^1 & \vec{\mathcal{V}}^2.\vec{n}^2 & \vec{\mathcal{V}}^2.\vec{n}^3 & \vec{\mathcal{V}}^2.\vec{n}^4 \\ \vec{\mathcal{V}}^3.\vec{n}^1 & \vec{\mathcal{V}}^3.\vec{n}^2 & \vec{\mathcal{V}}^3.\vec{n}^3 & \vec{\mathcal{V}}^3.\vec{n}^4 \\ \vec{\mathcal{V}}^4.\vec{n}^1 & \vec{\mathcal{V}}^4.\vec{n}^2 & \vec{\mathcal{V}}^4.\vec{n}^3 & \vec{\mathcal{V}}^4.\vec{n}^4 \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \\ c_i^4 \end{array} \right\} \tag{5}$$

2.1.3 Examples: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{array} \right\} = \left[\begin{array}{cccccccccccc} V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 & 0 & V^{14} & 0 & 0 \\ 0 & V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 & 0 & V^{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 & 0 & V^{24} & 0 & 0 \\ 0 & V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 & 0 & V^{24} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 & 0 & V^{34} & 0 & 0 \\ 0 & V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 & 0 & V^{34} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{41} & 0 & 0 & V^{42} & 0 & 0 & V^{43} & 0 & 0 & V^{44} & 0 & 0 \\ 0 & V^{41} & 0 & 0 & V^{42} & 0 & 0 & V^{43} & 0 & 0 & V^{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{array} \right\} \tag{6}$$

with

$$V^{mn} = \frac{\vec{\mathcal{V}}^m.\vec{n}^n}{1728}$$

2.2 Diffusion

2.2.1 Fluctuation in node

$$\begin{array}{rcl} \Delta c_i^m & = & \int_{V^m} \vec{\nabla}.\left(\sum_j D_{ij}\vec{\nabla}c_j\right) dV \\ & = & -\int_{\partial V^m} \left(\sum_j D_{ij}\vec{\nabla}c_j\right).d\vec{n} \end{array}$$

2.2.2 Element contribution to fluctuation in node

Assume that D_{ij} varies linearly.

$$\vec{\mathcal{D}}_{ij}^1 = 13\vec{n}^1 D_{ij}^1 + \left(7\vec{n}^1 - 2\vec{n}^2\right) D_{ij}^2 + \left(7\vec{n}^1 - 2\vec{n}^3\right) D_{ij}^3 + \left(7\vec{n}^1 - 2\vec{n}^4\right) D_{ij}^4$$

$$\vec{\mathcal{D}}_{ij}^2 = 13\vec{n}^2 D_{ij}^2 + \left(7\vec{n}^2 - 2\vec{n}^3\right) D_{ij}^3 + \left(7\vec{n}^2 - 2\vec{n}^4\right) D_{ij}^4 + \left(7\vec{n}^2 - 2\vec{n}^1\right) D_{ij}^1$$

$$\vec{\mathcal{D}}_{ij}^{3} = 13\vec{n}^{3} D_{ij}^{3} + \left(7\vec{n}^{3} - 2\vec{n}^{4}\right) D_{ij}^{4} + \left(7\vec{n}^{3} - 2\vec{n}^{1}\right) D_{ij}^{1} + \left(7\vec{n}^{3} - 2\vec{n}^{2}\right) D_{ij}^{2}$$

$$\vec{\mathcal{D}}_{ij}^{4} = 13\vec{n}^{3} D_{ij}^{4} + \left(7\vec{n}^{4} - 2\vec{n}^{1}\right) D_{ij}^{1} + \left(7\vec{n}^{4} - 2\vec{n}^{2}\right) D_{ij}^{2} + \left(7\vec{n}^{4} - 2\vec{n}^{3}\right) D_{ij}^{3}$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array} \right\} = -\frac{1}{324V} \sum_j \left[\begin{array}{cccc} \vec{\mathcal{D}}_{ij}^{1}.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^{1}.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^{1}.\vec{n}^3 & \vec{\mathcal{D}}_{ij}^{1}.\vec{n}^4 \\ \vec{\mathcal{D}}_{ij}^{2}.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^{2}.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^{2}.\vec{n}^3 & \vec{\mathcal{D}}_{ij}^{2}.\vec{n}^4 \\ \vec{\mathcal{D}}_{ij}^{3}.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^{3}.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^{3}.\vec{n}^3 & \vec{\mathcal{D}}_{ij}^{3}.\vec{n}^4 \\ \vec{\mathcal{D}}_{ij}^{4}.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^{4}.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^{4}.\vec{n}^3 & \vec{\mathcal{D}}_{ij}^{4}.\vec{n}^4 \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \\ c_j^3 \\ c_j^4 \end{array} \right\} \tag{7}$$

2.2.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{array} \right\} = \left[\begin{array}{cccccccccccc} D_{AA}^{11} & D_{AB}^{11} & 0 & D_{AA}^{12} & D_{AB}^{12} & 0 & D_{AA}^{13} & D_{AB}^{13} & 0 & D_{AA}^{14} & D_{AB}^{14} & 0 \\ D_{BA}^{11} & D_{BB}^{11} & 0 & D_{BA}^{12} & D_{BB}^{12} & 0 & D_{BA}^{13} & D_{BB}^{13} & 0 & D_{BA}^{14} & D_{BB}^{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ D_{AA}^{21} & D_{AB}^{21} & 0 & D_{AA}^{22} & D_{AB}^{22} & 0 & D_{AA}^{23} & D_{AB}^{23} & 0 & D_{AA}^{24} & D_{AB}^{24} & 0 \\ D_{BA}^{21} & D_{BB}^{21} & 0 & D_{BA}^{22} & D_{BB}^{22} & 0 & D_{BA}^{23} & D_{BB}^{23} & 0 & D_{BA}^{24} & D_{BB}^{24} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ D_{AA}^{31} & D_{AB}^{31} & 0 & D_{AA}^{32} & D_{AB}^{32} & 0 & D_{AA}^{33} & D_{AB}^{33} & 0 & D_{AA}^{34} & D_{AB}^{34} & 0 \\ D_{BA}^{31} & D_{BB}^{31} & 0 & D_{BA}^{32} & D_{BB}^{32} & 0 & D_{BA}^{33} & D_{BB}^{33} & 0 & D_{BA}^{34} & D_{BB}^{34} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ D_{AA}^{41} & D_{AB}^{41} & 0 & D_{AA}^{42} & D_{AB}^{42} & 0 & D_{AA}^{43} & D_{AB}^{43} & 0 & D_{AA}^{44} & D_{AB}^{44} & 0 \\ D_{BA}^{41} & D_{BB}^{41} & 0 & D_{BA}^{42} & D_{BB}^{42} & 0 & D_{BA}^{43} & D_{BB}^{43} & 0 & D_{BA}^{44} & D_{BB}^{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{array} \right\} \tag{8}$$

with

$$D_{ij}^{mn} = -\frac{\vec{\mathcal{D}}_{ij}^{m}.\vec{n}^n}{324V}$$

2.3 Migration

2.3.1 Fluctuation in node

$$\begin{aligned} \Delta c_i^m &= \int_{V^m} \vec{\nabla}.\left(w_i c_i \vec{\nabla} U\right) dV \\ &= -\int_{\partial V^m} \left(w_i c_i \vec{\nabla} U\right).d\vec{n} \end{aligned}$$

2.3.2 Element contribution to fluctuation in node

Assume that w_i varies linearly.

$$\vec{\mathcal{M}}_i^1 = \vec{\mathcal{W}}_i^{11} c_i^1 + \vec{\mathcal{W}}_i^{12} c_i^2 + \vec{\mathcal{W}}_i^{13} c_i^3 + \vec{\mathcal{W}}_i^{14} c_i^4$$

$$\vec{\mathcal{M}}_i^2 = \vec{\mathcal{W}}_i^{21} c_i^1 + \vec{\mathcal{W}}_i^{22} c_i^2 + \vec{\mathcal{W}}_i^{23} c_i^3 + \vec{\mathcal{W}}_i^{24} c_i^4$$

$$\vec{\mathcal{M}}_i^3 = \vec{\mathcal{W}}_i^{31} c_i^1 + \vec{\mathcal{W}}_i^{32} c_i^2 + \vec{\mathcal{W}}_i^{33} c_i^3 + \vec{\mathcal{W}}_i^{34} c_i^4$$

$$\vec{\mathcal{M}}_i^4 = \vec{\mathcal{W}}_i^{41} c_i^1 + \vec{\mathcal{W}}_i^{42} c_i^2 + \vec{\mathcal{W}}_i^{43} c_i^3 + \vec{\mathcal{W}}_i^{44} c_i^4$$

$$\vec{\mathcal{W}}_i^{11} = 230\vec{n}^1 w_i^1 + \left(119\vec{n}^1 - 37\vec{n}^2\right) w_i^2 + \left(119\vec{n}^1 - 37\vec{n}^3\right) w_i^3 + \left(119\vec{n}^1 - 37\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{12} = \left(119\vec{n}^1 - 37\vec{n}^2\right) w_i^1 + \left(92\vec{n}^1 - 46\vec{n}^2\right) w_i^2 + \left(69\vec{n}^1 + 13\vec{n}^4\right) w_i^3 + \left(69\vec{n}^1 + 13\vec{n}^3\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{13} = \left(119\vec{n}^1 - 37\vec{n}^3\right) w_i^1 + \left(69\vec{n}^1 + 13\vec{n}^4\right) w_i^2 + \left(92\vec{n}^1 - 46\vec{n}^3\right) w_i^3 + \left(69\vec{n}^1 + 13\vec{n}^2\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{14} = \left(119\vec{n}^1 - 37\vec{n}^4\right) w_i^1 + \left(69\vec{n}^1 + 13\vec{n}^3\right) w_i^2 + \left(69\vec{n}^1 + 13\vec{n}^2\right) w_i^3 + \left(92\vec{n}^1 - 46\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{21} = \left(92\vec{n}^2 - 46\vec{n}^1\right) w_i^1 + \left(119\vec{n}^2 - 37\vec{n}^1\right) w_i^2 + \left(69\vec{n}^2 + 13\vec{n}^4\right) w_i^3 + \left(69\vec{n}^2 + 13\vec{n}^3\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{22} = \left(119\vec{n}^2 - 37\vec{n}^1\right) w_i^1 + 230\vec{n}^2 w_i^2 + \left(119\vec{n}^2 - 37\vec{n}^3\right) w_i^3 + \left(119\vec{n}^2 - 37\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{23} = \left(69\vec{n}^2 + 13\vec{n}^4\right) w_i^1 + \left(119\vec{n}^2 - 37\vec{n}^3\right) w_i^2 + \left(92\vec{n}^2 - 46\vec{n}^3\right) w_i^3 + \left(69\vec{n}^2 + 13\vec{n}^1\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{24} = \left(69\vec{n}^2 + 13\vec{n}^3\right) w_i^1 + \left(119\vec{n}^2 - 37\vec{n}^4\right) w_i^2 + \left(69\vec{n}^2 + 13\vec{n}^1\right) w_i^3 + \left(92\vec{n}^2 - 46\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{31} = \left(92\vec{n}^3 - 46\vec{n}^1\right) w_i^1 + \left(69\vec{n}^3 + 13\vec{n}^4\right) w_i^2 + \left(119\vec{n}^3 - 37\vec{n}^1\right) w_i^3 + \left(69\vec{n}^3 + 13\vec{n}^2\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{32} = \left(69\vec{n}^3 + 13\vec{n}^4\right) w_i^1 + \left(92\vec{n}^3 - 46\vec{n}^2\right) w_i^2 + \left(119\vec{n}^3 - 37\vec{n}^2\right) w_i^3 + \left(69\vec{n}^3 + 13\vec{n}^1\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{33} = \left(119\vec{n}^3 - 37\vec{n}^1\right) w_i^1 + \left(119\vec{n}^3 - 37\vec{n}^2\right) w_i^2 + 230\vec{n}^3 w_i^3 + \left(119\vec{n}^3 - 37\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{34} = \left(69\vec{n}^3 + 13\vec{n}^2\right) w_i^1 + \left(69\vec{n}^3 + 13\vec{n}^1\right) w_i^2 + \left(119\vec{n}^3 - 37\vec{n}^4\right) w_i^3 + \left(92\vec{n}^3 - 46\vec{n}^4\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{41} = \left(92\vec{n}^4 - 46\vec{n}^1\right) w_i^1 + \left(69\vec{n}^4 + 13\vec{n}^3\right) w_i^2 + \left(69\vec{n}^4 + 13\vec{n}^2\right) w_i^3 + \left(119\vec{n}^4 - 37\vec{n}^1\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{42} = \left(69\vec{n}^4 + 13\vec{n}^3\right) w_i^1 + \left(92\vec{n}^4 - 46\vec{n}^2\right) w_i^2 + \left(69\vec{n}^4 + 13\vec{n}^1\right) w_i^3 + \left(119\vec{n}^4 - 37\vec{n}^2\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{43} = \left(69\vec{n}^4 + 13\vec{n}^2\right) w_i^1 + \left(69\vec{n}^4 + 13\vec{n}^1\right) w_i^2 + \left(92\vec{n}^4 - 46\vec{n}^3\right) w_i^3 + \left(119\vec{n}^4 - 37\vec{n}^3\right) w_i^4$$

$$\vec{\mathcal{W}}_i^{44} = \left(119\vec{n}^4 - 37\vec{n}^1\right) w_i^1 + \left(119\vec{n}^4 - 37\vec{n}^2\right) w_i^2 + \left(119\vec{n}^4 - 37\vec{n}^3\right) w_i^3 + 230\vec{n}^4 w_i^4$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array} \right\} = -\frac{1}{15552V} \left[\begin{array}{cccc} \vec{\mathcal{M}}_i^1.\vec{n}^1 & \vec{\mathcal{M}}_i^1.\vec{n}^2 & \vec{\mathcal{M}}_i^1.\vec{n}^3 & \vec{\mathcal{M}}_i^1.\vec{n}^4 \\ \vec{\mathcal{M}}_i^2.\vec{n}^1 & \vec{\mathcal{M}}_i^2.\vec{n}^2 & \vec{\mathcal{M}}_i^2.\vec{n}^3 & \vec{\mathcal{M}}_i^2.\vec{n}^4 \\ \vec{\mathcal{M}}_i^3.\vec{n}^1 & \vec{\mathcal{M}}_i^3.\vec{n}^2 & \vec{\mathcal{M}}_i^3.\vec{n}^3 & \vec{\mathcal{M}}_i^3.\vec{n}^4 \\ \vec{\mathcal{M}}_i^4.\vec{n}^1 & \vec{\mathcal{M}}_i^4.\vec{n}^2 & \vec{\mathcal{M}}_i^4.\vec{n}^3 & \vec{\mathcal{M}}_i^4.\vec{n}^4 \end{array} \right] \left\{ \begin{array}{c} U^1 \\ U^2 \\ U^3 \\ U^4 \end{array} \right\} \tag{9}$$

2.3.3 Example: binary electrolyte

$$\begin{Bmatrix} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{Bmatrix} = \begin{bmatrix} 0 & 0 & M_A^{11} & 0 & 0 & M_A^{12} & 0 & 0 & M_A^{13} & 0 & 0 & M_A^{14} \\ 0 & 0 & M_B^{11} & 0 & 0 & M_B^{12} & 0 & 0 & M_B^{13} & 0 & 0 & M_B^{14} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{21} & 0 & 0 & M_A^{22} & 0 & 0 & M_A^{23} & 0 & 0 & M_A^{24} \\ 0 & 0 & M_B^{21} & 0 & 0 & M_B^{22} & 0 & 0 & M_B^{23} & 0 & 0 & M_B^{24} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{31} & 0 & 0 & M_A^{32} & 0 & 0 & M_A^{33} & 0 & 0 & M_A^{34} \\ 0 & 0 & M_B^{31} & 0 & 0 & M_B^{32} & 0 & 0 & M_B^{33} & 0 & 0 & M_B^{34} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{41} & 0 & 0 & M_A^{42} & 0 & 0 & M_A^{43} & 0 & 0 & M_A^{44} \\ 0 & 0 & M_B^{41} & 0 & 0 & M_B^{42} & 0 & 0 & M_B^{43} & 0 & 0 & M_B^{44} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{Bmatrix} \tag{10}$$

with

$$M_i^{mn} = -\frac{\vec{\mathcal{M}}_A^m . \vec{n}^n}{15552V}$$

2.4 Homogeneous reactions

2.4.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

- Monomolecular

$$v = kc_j$$

$$\Delta c_i^m = \int_{V^m} kc_j dV$$

- Bimolecular

$$v = kc_j c_k$$

$$\Delta c_i^m = \int_{V^m} kc_j c_k dV$$

2.4.2 Element contribution to fluctuation in node

Assume that k varies linearly.

- Monomolecular

$$\mathcal{H}_j^{11} = 1245k^1 + 335k^2 + 335k^3 + 335k^4$$

$$\mathcal{H}_j^{12} = 335k^1 + 161k^2 + 97k^3 + 97k^4$$

$$\mathcal{H}_j^{13} = 335k^1 + 97k^2 + 161k^3 + 97k^4$$

$$\mathcal{H}_j^{14} = 335k^1 + 97k^2 + 97k^3 + 161k^4$$

$$\mathcal{H}_j^{21} = 161k^1 + 335k^2 + 97k^3 + 97k^4$$

$$\mathcal{H}_j^{22} = 335k^1 + 1245k^2 + 335k^3 + 335k^4$$

$$\mathcal{H}_j^{23} = 97k^1 + 335k^2 + 161k^3 + 97k^4$$

$$\mathcal{H}_j^{24} = 97k^1 + 335k^2 + 97k^3 + 161k^4$$

$$\mathcal{H}_j^{31} = 161k^1 + 97k^2 + 335k^3 + 97k^4$$

$$\mathcal{H}_j^{32} = 97k^1 + 161k^2 + 335k^3 + 97k^4$$

$$\mathcal{H}_j^{33} = 335k^1 + 335k^2 + 1245k^3 + 335k^4$$

$$\mathcal{H}_j^{34} = 97k^1 + 97k^2 + 335k^3 + 161k^4$$

$$\mathcal{H}_j^{41} = 161k^1 + 97k^2 + 97k^3 + 335k^4$$

$$\mathcal{H}_j^{42} = 97k^1 + 161k^2 + 97k^3 + 335k^4$$

$$\mathcal{H}_j^{43} = 97k^1 + 97k^2 + 161k^3 + 335k^4$$

$$\mathcal{H}_j^{44} = 335k^1 + 335k^2 + 335k^3 + 1245k^4$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array} \right\} = \frac{V}{17280} \left[\begin{array}{cccc} \mathcal{H}_j^{11} & \mathcal{H}_j^{12} & \mathcal{H}_j^{13} & \mathcal{H}_j^{14} \\ \mathcal{H}_j^{21} & \mathcal{H}_j^{22} & \mathcal{H}_j^{23} & \mathcal{H}_j^{24} \\ \mathcal{H}_j^{31} & \mathcal{H}_j^{32} & \mathcal{H}_j^{33} & \mathcal{H}_j^{34} \\ \mathcal{H}_j^{41} & \mathcal{H}_j^{42} & \mathcal{H}_j^{43} & \mathcal{H}_j^{44} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \\ c_j^3 \\ c_j^4 \end{array} \right\} \tag{11}$$

- Bimolecular

$$\mathcal{K}^{111} = 17535k^1 + 4115k^2 + 4115k^3 + 4115k^4$$

$$\mathcal{K}^{222} = 4115k^1 + 17535k^2 + 4115k^3 + 4115k^4$$

$$\mathcal{K}^{333} = 4115k^1 + 4115k^2 + 17535k^3 + 4115k^4$$

$$\mathcal{K}^{444} = 4115k^1 + 4115k^2 + 4115k^3 + 17535k^4$$

$$\mathcal{K}^{112} = \mathcal{K}^{121} = 4115k^1 + 1815k^2 + 1055k^3 + 1055k^4$$

$$\mathcal{K}^{113} = \mathcal{K}^{131} = 4115k^1 + 1055k^2 + 1815k^3 + 1055k^4$$

$$\mathcal{K}^{114} = \mathcal{K}^{141} = 4115k^1 + 1055k^2 + 1055k^3 + 1815k^4$$

$$\mathcal{K}^{212} = \mathcal{K}^{221} = 1815k^1 + 4115k^2 + 1055k^3 + 1055k^4$$

$$\mathcal{K}^{223} = \mathcal{K}^{232} = 1055k^1 + 4115k^2 + 1815k^3 + 1055k^4$$

$$\mathcal{K}^{224} = \mathcal{K}^{242} = 1055k^1 + 4115k^2 + 1055k^3 + 1815k^4$$

$$\mathcal{K}^{331} = \mathcal{K}^{313} = 1815k^1 + 1055k^2 + 4115k^3 + 1055k^4$$

$$\mathcal{K}^{332} = \mathcal{K}^{323} = 1055k^1 + 1815k^2 + 4115k^3 + 1055k^4$$

$$\mathcal{K}^{334} = \mathcal{K}^{343} = 1055k^1 + 1055k^2 + 4115k^3 + 1815k^4$$

$$\mathcal{K}^{441} = \mathcal{K}^{414} = 1815k^1 + 1055k^2 + 1055k^3 + 4115k^4$$

$$\mathcal{K}^{442} = \mathcal{K}^{424} = 1055k^1 + 1815k^2 + 1055k^3 + 4115k^4$$

$$\mathcal{K}^{443} = \mathcal{K}^{434} = 1055k^1 + 1055k^2 + 1815k^3 + 4115k^4$$

$$\mathcal{K}^{122} = 1815k^1 + 1067k^2 + 491k^3 + 491k^4$$

$$\mathcal{K}^{133} = 1815k^1 + 491k^2 + 1067k^3 + 491k^4$$

$$\mathcal{K}^{144} = 1815k^1 + 491k^2 + 491k^3 + 1067k^4$$

$$\mathcal{K}^{211} = 1067k^1 + 1815k^2 + 491k^3 + 491k^4$$

$$\mathcal{K}^{233} = 491k^1 + 1815k^2 + 1067k^3 + 491k^4$$

$$\mathcal{K}^{244} = 491k^1 + 1815k^2 + 491k^3 + 1067k^4$$

$$\mathcal{K}^{311} = 1067k^1 + 491k^2 + 1815k^3 + 491k^4$$

$$\mathcal{K}^{322} = 491k^1 + 1067k^2 + 1815k^3 + 491k^4$$

$$\mathcal{K}^{344} = 491k^1 + 491k^2 + 1815k^3 + 1067k^4$$

$$\mathcal{K}^{411} = 1067k^1 + 491k^2 + 491k^3 + 1815k^4$$

$$\mathcal{K}^{422} = 491k^1 + 1067k^2 + 491k^3 + 1815k^4$$

$$\mathcal{K}^{433} = 491k^1 + 491k^2 + 1067k^3 + 1815k^4$$

$$\mathcal{K}^{123} = \mathcal{K}^{132} = 1055k^1 + 491k^2 + 491k^3 + 291k^4$$

$$\mathcal{K}^{124} = \mathcal{K}^{142} = 1055k^1 + 491k^2 + 291k^3 + 491k^4$$

$$\mathcal{K}^{134} = \mathcal{K}^{143} = 1055k^1 + 291k^2 + 491k^3 + 491k^4$$

$$\mathcal{K}^{213} = \mathcal{K}^{231} = 491k^1 + 1055k^2 + 491k^3 + 291k^4$$

$$\mathcal{K}^{214} = \mathcal{K}^{241} = 491k^1 + 1055k^2 + 291k^3 + 491k^4$$

$$\mathcal{K}^{234} = \mathcal{K}^{243} = 291k^1 + 1055k^2 + 491k^3 + 491k^4$$

$$\mathcal{K}^{312} = \mathcal{K}^{321} = 491k^1 + 491k^2 + 1055k^3 + 291k^4$$

$$\mathcal{K}^{314} = \mathcal{K}^{341} = 491k^1 + 291k^2 + 1055k^3 + 491k^4$$

$$\mathcal{K}^{324} = \mathcal{K}^{342} = 291k^1 + 491k^2 + 1055k^3 + 491k^4$$

$$\mathcal{K}^{412} = \mathcal{K}^{421} = 491k^1 + 491k^2 + 291k^3 + 1055k^4$$

$$\mathcal{K}^{413} = \mathcal{K}^{431} = 491k^1 + 291k^2 + 491k^3 + 1055k^4$$

$$\mathcal{K}^{423} = \mathcal{K}^{432} = 291k^1 + 491k^2 + 491k^3 + 1055k^4$$

$$\mathcal{H}_j^{11} = \mathcal{K}^{111}c_k^1 + \mathcal{K}^{112}c_k^2 + \mathcal{K}^{113}c_k^3 + \mathcal{K}^{114}c_k^4$$

$$\mathcal{H}_j^{12} = \mathcal{K}^{121}c_k^1 + \mathcal{K}^{122}c_k^2 + \mathcal{K}^{123}c_k^3 + \mathcal{K}^{124}c_k^4$$

$$\mathcal{H}_j^{13} = \mathcal{K}^{131}c_k^1 + \mathcal{K}^{132}c_k^2 + \mathcal{K}^{133}c_k^3 + \mathcal{K}^{134}c_k^4$$

$$\mathcal{H}_j^{14} = \mathcal{K}^{141}c_k^1 + \mathcal{K}^{142}c_k^2 + \mathcal{K}^{143}c_k^3 + \mathcal{K}^{144}c_k^4$$

$$\mathcal{H}_j^{21} = \mathcal{K}^{211}c_k^1 + \mathcal{K}^{212}c_k^2 + \mathcal{K}^{213}c_k^3 + \mathcal{K}^{214}c_k^4$$

$$\mathcal{H}_j^{22} = \mathcal{K}^{221}c_k^1 + \mathcal{K}^{222}c_k^2 + \mathcal{K}^{223}c_k^3 + \mathcal{K}^{224}c_k^4$$

$$\mathcal{H}_j^{23} = \mathcal{K}^{231}c_k^1 + \mathcal{K}^{232}c_k^2 + \mathcal{K}^{233}c_k^3 + \mathcal{K}^{234}c_k^4$$

$$\mathcal{H}_j^{24} = \mathcal{K}^{241}c_k^1 + \mathcal{K}^{242}c_k^2 + \mathcal{K}^{243}c_k^3 + \mathcal{K}^{244}c_k^4$$

$$\mathcal{H}_j^{31} = \mathcal{K}^{311}c_k^1 + \mathcal{K}^{312}c_k^2 + \mathcal{K}^{313}c_k^3 + \mathcal{K}^{314}c_k^4$$

$$\mathcal{H}_j^{32} = \mathcal{K}^{321}c_k^1 + \mathcal{K}^{322}c_k^2 + \mathcal{K}^{323}c_k^3 + \mathcal{K}^{324}c_k^4$$

$$\mathcal{H}_j^{33} = \mathcal{K}^{331}c_k^1 + \mathcal{K}^{332}c_k^2 + \mathcal{K}^{333}c_k^3 + \mathcal{K}^{334}c_k^4$$

$$\mathcal{H}_j^{34} = \mathcal{K}^{341}c_k^1 + \mathcal{K}^{342}c_k^2 + \mathcal{K}^{343}c_k^3 + \mathcal{K}^{344}c_k^4$$

$$\mathcal{H}_j^{41} = \mathcal{K}^{411}c_k^1 + \mathcal{K}^{412}c_k^2 + \mathcal{K}^{413}c_k^3 + \mathcal{K}^{414}c_k^4$$

$$\mathcal{H}_j^{42} = \mathcal{K}^{421}c_k^1 + \mathcal{K}^{422}c_k^2 + \mathcal{K}^{423}c_k^3 + \mathcal{K}^{424}c_k^4$$

$$\mathcal{H}_j^{43} = \mathcal{K}^{431}c_k^1 + \mathcal{K}^{432}c_k^2 + \mathcal{K}^{433}c_k^3 + \mathcal{K}^{434}c_k^4$$

$$\mathcal{H}_j^{44} = \mathcal{K}^{441}c_k^1 + \mathcal{K}^{442}c_k^2 + \mathcal{K}^{443}c_k^3 + \mathcal{K}^{444}c_k^4$$

$$\left\{\begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array}\right\} = \frac{V}{829440}\left[\begin{array}{cccccccc} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13} & \mathcal{H}_j^{14} & \mathcal{H}_k^{14} \\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23} & \mathcal{H}_j^{24} & \mathcal{H}_k^{24} \\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33} & \mathcal{H}_j^{34} & \mathcal{H}_k^{34} \\ \mathcal{H}_j^{41} & \mathcal{H}_k^{41} & \mathcal{H}_j^{42} & \mathcal{H}_k^{42} & \mathcal{H}_j^{43} & \mathcal{H}_k^{43} & \mathcal{H}_j^{44} & \mathcal{H}_k^{44} \end{array}\right]\left\{\begin{array}{c} c_j^1 \\ c_k^1 \\ c_j^2 \\ c_k^2 \\ c_j^3 \\ c_k^3 \\ c_j^4 \\ c_k^4 \end{array}\right\} \tag{12}$$

2.4.3 Example: monomolecular-monomolecular reversible reaction $A \rightleftharpoons B$

$$v = k_f c_A - k_b c_B$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{array}\right\} = \left[\begin{array}{cccccccccccc} -H_A^{11} & H_B^{11} & 0 & -H_A^{12} & H_B^{12} & 0 & -H_A^{13} & H_B^{13} & 0 & -H_A^{14} & H_B^{14} & 0 \\ H_A^{11} & -H_B^{11} & 0 & H_A^{12} & -H_B^{12} & 0 & H_A^{13} & -H_B^{13} & 0 & H_A^{14} & -H_B^{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{21} & H_B^{21} & 0 & -H_A^{22} & H_B^{22} & 0 & -H_A^{23} & H_B^{23} & 0 & -H_A^{24} & H_B^{24} & 0 \\ H_A^{21} & -H_B^{21} & 0 & H_A^{22} & -H_B^{22} & 0 & H_A^{23} & -H_B^{23} & 0 & H_A^{24} & -H_B^{24} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{31} & H_B^{31} & 0 & -H_A^{32} & H_B^{32} & 0 & -H_A^{33} & H_B^{33} & 0 & -H_A^{34} & H_B^{34} & 0 \\ H_A^{31} & -H_B^{31} & 0 & H_A^{32} & -H_B^{32} & 0 & H_A^{33} & -H_B^{33} & 0 & H_A^{34} & -H_B^{34} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{41} & H_B^{41} & 0 & -H_A^{42} & H_B^{42} & 0 & -H_A^{43} & H_B^{43} & 0 & -H_A^{44} & H_B^{44} & 0 \\ H_A^{41} & -H_B^{41} & 0 & H_A^{42} & -H_B^{42} & 0 & H_A^{43} & -H_B^{43} & 0 & H_A^{44} & -H_B^{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right]\left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{array}\right\} \tag{13}$$

with for the forward reaction (replace k by k_f in the formulae!)

$$H_A^{mn} = \frac{V}{17280}\mathcal{H}_A^{mn}$$

and for the backward reaction (replace k by k_b in the formulae!)

$$H_B^{mn} = \frac{V}{17280}\mathcal{H}_B^{mn}$$

2.5 Poisson's equation

2.5.1 Fluctuation in node

$$\begin{aligned} \Delta U^m &= \int_{V^m} \vec{\nabla}^2 U dV + \int_{V^m} \tfrac{F}{\epsilon} \sum_i z_i c_i dV \\ &= -\int_{\partial V^m} \vec{\nabla} U . d\vec{n} + \sum_i \tfrac{z_i F}{\epsilon} \int_{V^m} c_i dV \end{aligned}$$

2.5.2 Element contribution to fluctuation in node

$$\left\{ \begin{array}{c} \Delta U^1 \\ \Delta U^2 \\ \Delta U^3 \\ \Delta U^4 \end{array} \right\} = \left[\begin{array}{cccccccc} \frac{75V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^1}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^2}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^3}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^4}{12V} \\ \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^1}{12V} & \frac{75V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^2}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^3}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^4}{12V} \\ \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^1}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^2}{12V} & \frac{75V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^3}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^4}{12V} \\ \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^4.\vec{n}^1}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^4.\vec{n}^2}{12V} & \frac{23V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^4.\vec{n}^3}{12V} & \frac{75V}{576}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^4.\vec{n}^4}{12V} \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ U^1 \\ c_i^2 \\ U^2 \\ c_i^3 \\ U^3 \\ c_i^4 \\ U^4 \end{array} \right\} \tag{14}$$

2.5.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{array} \right\} = \left[\begin{array}{cccccccccccc} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 75Z_A & 75Z_B & n^{11} & 23Z_A & 23Z_B & n^{12} & 23Z_A & 23Z_B & n^{13} & 23Z_A & 23Z_B & n^{14} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 23Z_A & 23Z_B & n^{21} & 75Z_A & 75Z_B & n^{22} & 23Z_A & 23Z_B & n^{23} & 23Z_A & 23Z_B & n^{24} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 23Z_A & 23Z_B & n^{31} & 23Z_A & 23Z_B & n^{32} & 75Z_A & 75Z_B & n^{33} & 23Z_A & 23Z_B & n^{34} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 23Z_A & 23Z_B & n^{41} & 23Z_A & 23Z_B & n^{42} & 23Z_A & 23Z_B & n^{43} & 75Z_A & 75Z_B & n^{44} \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{array} \right\} \tag{15}$$

with

$$Z_i = \frac{V}{576}\frac{z_iF}{\epsilon}$$

$$n^{mn} = -\frac{\vec{n}^m.\vec{n}^n}{12V}$$

2.6 Time

2.6.1 Fluctuation in node

$$\Delta c_i^m = \int_{V^m} \frac{\partial c_i}{\partial t} dV$$

2.6.2 Element contribution to fluctuation in node

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array} \right\} = \frac{V}{576} \left[\begin{array}{cccc} 75 & 7 & 7 & 7 \\ 7 & 75 & 7 & 7 \\ 7 & 7 & 75 & 7 \\ 7 & 7 & 7 & 75 \end{array} \right] \left\{ \begin{array}{c} \frac{\partial c_i^1}{\partial t} \\ \frac{\partial c_i^2}{\partial t} \\ \frac{\partial c_i^3}{\partial t} \\ \frac{\partial c_i^4}{\partial t} \end{array} \right\} \tag{16}$$

3 Boundary element vector

3.1 Electrode reactions

3.1.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V - U)\right] c_{red} - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V - U)\right] c_{ox}$$

$$\Delta c_i^m = \int_{S^m} R_i dS$$

3.1.2 Boundary element contribution to fluctuation in node

Assume that the normal flux varies linearly on the boundary.

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{108} \left\{ \begin{array}{c} 22R_i^1 + 7R_i^2 + 7R_i^3 \\ 7R_i^1 + 22R_i^2 + 7R_i^3 \\ 7R_i^1 + 7R_i^2 + 22R_i^3 \end{array} \right\} \tag{17}$$

3.1.3 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V - U)\right] c_B - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V - U)\right] c_A$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array}\right\} = \left\{\begin{array}{c} -\frac{S}{108}\left(22N_i^1 + 7N_i^2 + 7N_i^3\right) \\ \frac{S}{108}\left(22N_i^1 + 7N_i^2 + 7N_i^3\right) \\ 0 \\ -\frac{S}{108}\left(7N_i^1 + 22N_i^2 + 7N_i^3\right) \\ \frac{S}{108}\left(7N_i^1 + 22N_i^2 + 7N_i^3\right) \\ 0 \\ -\frac{S}{108}\left(7N_i^1 + 7N_i^2 + 22N_i^3\right) \\ \frac{S}{108}\left(7N_i^1 + 7N_i^2 + 22N_i^3\right) \\ 0 \end{array}\right\} \tag{18}$$

4 Element jacobian

4.1 Convection

Zero contribution.

4.2 Diffusion

Zero contribution (approximately).

4.3 Migration

4.3.1 Element contribution to fluctuation in node

$$\vec{\nabla} U = \frac{\vec{n}^1 U^1 + \vec{n}^2 U^2 + \vec{n}^3 U^3 + \vec{n}^4 U^4}{3V}$$

$$\left\{\begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array}\right\} = -\frac{\vec{\nabla} U}{5184} . \left[\begin{array}{cccc} \vec{\mathcal{W}}_i^{11} & \vec{\mathcal{W}}_i^{12} & \vec{\mathcal{W}}_i^{13} & \vec{\mathcal{W}}_i^{14} \\ \vec{\mathcal{W}}_i^{21} & \vec{\mathcal{W}}_i^{22} & \vec{\mathcal{W}}_i^{23} & \vec{\mathcal{W}}_i^{24} \\ \vec{\mathcal{W}}_i^{31} & \vec{\mathcal{W}}_i^{32} & \vec{\mathcal{W}}_i^{33} & \vec{\mathcal{W}}_i^{34} \\ \vec{\mathcal{W}}_i^{41} & \vec{\mathcal{W}}_i^{42} & \vec{\mathcal{W}}_i^{43} & \vec{\mathcal{W}}_i^{44} \end{array}\right] \left\{\begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \\ c_i^4 \end{array}\right\} \tag{19}$$

4.3.2 Example: binary electrolyte

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \\ \Delta c_A^4 \\ \Delta c_B^4 \\ \Delta U^4 \end{array}\right\} = \left[\begin{array}{cccccccccccc} \tilde{M}_A^{11} & 0 & 0 & \tilde{M}_A^{12} & 0 & 0 & \tilde{M}_A^{13} & 0 & 0 & \tilde{M}_A^{14} & 0 & 0 \\ 0 & \tilde{M}_B^{11} & 0 & 0 & \tilde{M}_B^{12} & 0 & 0 & \tilde{M}_B^{13} & 0 & 0 & \tilde{M}_B^{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{M}_A^{21} & 0 & 0 & \tilde{M}_A^{22} & 0 & 0 & \tilde{M}_A^{23} & 0 & 0 & \tilde{M}_A^{24} & 0 & 0 \\ 0 & \tilde{M}_B^{21} & 0 & 0 & \tilde{M}_B^{22} & 0 & 0 & \tilde{M}_B^{23} & 0 & 0 & \tilde{M}_B^{24} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{M}_A^{31} & 0 & 0 & \tilde{M}_A^{32} & 0 & 0 & \tilde{M}_A^{33} & 0 & 0 & \tilde{M}_A^{34} & 0 & 0 \\ 0 & \tilde{M}_B^{31} & 0 & 0 & \tilde{M}_B^{32} & 0 & 0 & \tilde{M}_B^{33} & 0 & 0 & \tilde{M}_B^{34} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{M}_A^{41} & 0 & 0 & \tilde{M}_A^{42} & 0 & 0 & \tilde{M}_A^{43} & 0 & 0 & \tilde{M}_A^{44} & 0 & 0 \\ 0 & \tilde{M}_B^{41} & 0 & 0 & \tilde{M}_B^{42} & 0 & 0 & \tilde{M}_B^{43} & 0 & 0 & \tilde{M}_B^{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \\ c_A^4 \\ c_B^4 \\ U^4 \end{array}\right\} \tag{20}$$

with

$$\tilde{M}_i^{mn} = -\vec{\nabla} U . \frac{\vec{\mathcal{W}}_i^{mn}}{5184}$$

4.4 Homogeneous reactions

4.4.1 Element contribution to fluctuation in node

- Monomolecular

Zero contribution (approximately).

- Bimolecular

Because of the symmetry it is the same contribution.

$$\left\{\begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \\ \Delta c_i^4 \end{array}\right\} = \frac{V}{829440} \left[\begin{array}{cccccccc} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13} & \mathcal{H}_j^{14} & \mathcal{H}_k^{14} \\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23} & \mathcal{H}_j^{24} & \mathcal{H}_k^{24} \\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33} & \mathcal{H}_j^{34} & \mathcal{H}_k^{34} \\ \mathcal{H}_j^{41} & \mathcal{H}_k^{41} & \mathcal{H}_j^{42} & \mathcal{H}_k^{42} & \mathcal{H}_j^{43} & \mathcal{H}_k^{43} & \mathcal{H}_j^{44} & \mathcal{H}_k^{44} \end{array}\right] \left\{\begin{array}{c} c_j^1 \\ c_k^1 \\ c_j^2 \\ c_k^2 \\ c_j^3 \\ c_k^3 \\ c_j^4 \\ c_k^4 \end{array}\right\} \tag{21}$$

4.5 Poisson's equation

Zero contribution.

4.6 Time

Zero contribution.

5 Boundary element jacobian

5.1 Electrode reactions

5.1.1 Partial derivatives

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox} nF}{RT} k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_{red} - \frac{\alpha_{red} nF}{RT} k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_{ox}$$

$$\frac{\partial v}{\partial c_{ox}} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_{red}} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{108} \left[\begin{array}{cccccc} 22\frac{\partial R_i^1}{\partial c_j^1} & 22\frac{\partial R_i^1}{\partial U^1} & 7\frac{\partial R_i^2}{\partial c_j^2} & 7\frac{\partial R_i^2}{\partial U^2} & 7\frac{\partial R_i^3}{\partial c_j^3} & 7\frac{\partial R_i^3}{\partial U^3} \\ 7\frac{\partial R_i^1}{\partial c_j^1} & 7\frac{\partial R_i^1}{\partial U^1} & 22\frac{\partial R_i^2}{\partial c_j^2} & 22\frac{\partial R_i^2}{\partial U^2} & 7\frac{\partial R_i^3}{\partial c_j^3} & 7\frac{\partial R_i^3}{\partial U^3} \\ 7\frac{\partial R_i^1}{\partial c_j^1} & 7\frac{\partial R_i^1}{\partial U^1} & 7\frac{\partial R_i^2}{\partial c_j^2} & 7\frac{\partial R_i^2}{\partial U^2} & 22\frac{\partial R_i^3}{\partial c_j^3} & 22\frac{\partial R_i^3}{\partial U^3} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ U^1 \\ c_j^2 \\ U^2 \\ c_j^3 \\ U^3 \end{array} \right\} \tag{22}$$

5.1.2 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox} nF}{RT} k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - \frac{\alpha_{red} nF}{RT} k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$\frac{\partial v}{\partial c_A} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_B} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} -22\tilde{C}_A^1 & -22\tilde{C}_B^1 & -22\tilde{U}^1 & -7\tilde{C}_A^2 & -7\tilde{C}_B^2 & -7\tilde{U}^2 & -7\tilde{C}_A^3 & -7\tilde{C}_B^3 & -7\tilde{U}^3 \\ 22\tilde{C}_A^1 & 22\tilde{C}_B^1 & 22\tilde{U}^1 & 7\tilde{C}_A^2 & 7\tilde{C}_B^2 & 7\tilde{U}^2 & 7\tilde{C}_A^3 & 7\tilde{C}_B^3 & 7\tilde{U}^3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -7\tilde{C}_A^1 & -7\tilde{C}_B^1 & -7\tilde{U}^1 & -22\tilde{C}_A^2 & -22\tilde{C}_B^2 & -22\tilde{U}^2 & -7\tilde{C}_A^3 & -7\tilde{C}_B^3 & -7\tilde{U}^3 \\ 7\tilde{C}_A^1 & 7\tilde{C}_B^1 & 7\tilde{U}^1 & 22\tilde{C}_A^2 & 22\tilde{C}_B^2 & 22\tilde{U}^2 & 7\tilde{C}_A^3 & 7\tilde{C}_B^3 & 7\tilde{U}^3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -7\tilde{C}_A^1 & -7\tilde{C}_B^1 & -7\tilde{U}^1 & -7\tilde{C}_A^2 & -7\tilde{C}_B^2 & -7\tilde{U}^2 & -22\tilde{C}_A^3 & -22\tilde{C}_B^3 & -22\tilde{U}^3 \\ 7\tilde{C}_A^1 & 7\tilde{C}_B^1 & 7\tilde{U}^1 & 7\tilde{C}_A^2 & 7\tilde{C}_B^2 & 7\tilde{U}^2 & 22\tilde{C}_A^3 & 22\tilde{C}_B^3 & 22\tilde{U}^3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{23}$$

with

$$\tilde{C}_i^m = \frac{S}{108} \frac{\partial v^m}{\partial c_i^m}$$

$$\tilde{U}^m = \frac{S}{108} \frac{\partial v^m}{\partial U^m}$$